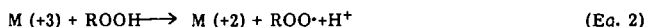
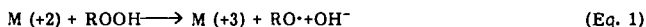


## The Catalytic Activity of Transition Metal Complexes in Oxidation Reactions Utilizing Hydroperoxides

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### INTRODUCTION

Hydroperoxides and oxy-based radicals have often been identified as residue and color formation precursors in hydrocarbon fuels during storage<sup>1</sup>. Typically the peroxides are generated during the propagation step of an air autoxidation mechanism and their formation is continuous as long as initiators and oxygen are present for the reaction to occur. A study performed in jet fuel determined that the square root of peroxide concentration is proportional to fuel storage duration<sup>2</sup>. The peroxide species, once formed in the fuel, have a wide range of possible reactions in which they can participate. For example, the reaction with olefins<sup>3</sup>, nitrogen compounds<sup>4</sup> and sulfur compounds<sup>5</sup> present in the hydrocarbon yields epoxides, amine oxides or nitro compounds, and disulfides, sulfoxides, sulfones, etc., respectively. The reactivity of the peroxide species toward the above derivatives can be modified in a number of ways. One of the more common methods is the introduction of a metal catalyst. The metal, when present even in catalytic amounts, may cause rapid degradation of the peroxides into oxy or peroxy radicals<sup>6</sup>.



The formation of esters, olefins or even alkyl halides is possible depending on the catalyst present, its oxidation state and the counter ion associated with it<sup>7</sup>. Vanadium complexes for example have been shown to be excellent catalysts for the oxidation of tertiary amines to amine oxides<sup>8</sup>. Iron and cobalt were found to be poor catalysts for the same reaction. Phenols have also been shown to be oxidatively unstable in fuels<sup>9</sup> yielding an additional reagent for the peroxides to interact with in these systems.

A factor which has not been as widely studied is the influence of ligands on the catalytic activity of the metal<sup>10</sup>. When the metal is in a mid-distillate, there are a variety of nitrogen and sulfur, etc., species present to act as ligands to complex the metal. The complex may have a much different redox potential than the metal itself as well as having ligands blocking potential coordination sites for the peroxide and thereby preventing its decomposition from occurring.

A study was thus conducted to investigate the influence various ligands have on the oxidation of olefins and phenols by hydroperoxides in the presence of various metal catalysts. The reactions were investigated without added solvent as well as in a No. 2

diesel fuel to determine if the reactivity was similar or if other fuel components present in the hydrocarbon would alter the results. Reactions were conducted under conditions commonly used for mid-distillate fuel stability testing.

## EXPERIMENTAL

In the cyclohexene oxidation studies, samples were prepared using 0.1 mole cyclohexene, 0.1 mole 90% tert-butyl hydroperoxide,  $1 \times 10^{-3}$  mole metal catalyst and  $5 \times 10^{-3}$  mole of the ligand where applicable. The samples were heated at the specified temperature for the desired time period and then analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Varian Gemini 300) and by GC mass spectroscopy (DuPont DP-1 mass spectrometer). Product yields were determined by capillary GC (HP-5710A). Fuel studies utilized the above amounts of dopants added to a 300 mL sample. All samples were stirred until homogeneous and then stored in an oven at  $43^\circ\text{C}$  until analyzed for residue content as specified in ASTM D-4625.

Experiments for phenol oxidation were performed using 0.1 mole p-cresol, 0.1 mole 90% tert-butyl hydroperoxide,  $1 \times 10^{-3}$  mole catalyst and  $5 \times 10^{-3}$  mole ligand. Product yield was determined by gas chromatography after conversion of the phenol mixture to their methyl ethers by treatment with  $\text{Me}_4\text{NOH}$  and  $\text{MeI}$  to increase their volatility. Fuel studies were run using 1000 ppm p-cresol and hydroperoxide, 1 ppm metal catalyst and 5 ppm ligand. The p-cresol, cyclohexene, tert-butyl hydroperoxide and the metal catalysts, cobalt acetate monohydrate ( $\text{Co}(\text{OAc})_2$ ), copper acetate tetrahydrate ( $\text{Cu}(\text{OAc})_2$ ), nickel acetate tetrahydrate ( $\text{Ni}(\text{OAc})_2$ ), vanadium pentoxide, anhydrous ferric chloride and the ligands pyridine and tetrahydrothiophene (THT) were purchased from Aldrich Chemical Co. and used as received. The ligands chelant 1 and chelant 2 are proprietary commercial metal chelants used as mid-distillate fuel stability additives. Fuel utilized in the studies was a No. 2 diesel fuel produced at a Gulf Coast refinery containing a 80/20 mixture of straight run distillate and LCO.

## RESULTS

Analysis of the cyclohexene oxidation products present after heating, indicated each contained a complex mixture of tert-butanol, acetone, cyclohexene, 2-cyclohexene-1-ol, 2-cyclohexene-1-one, tert-butoxy-2-cyclohexene and 2-cyclohexenyl-tert-butyl peroxide. The wide variety of products is indicative of the complexity of the reaction and of the many different reaction mechanisms available for the peroxides and radicals. The ether and peroxide products formed by oxidation of cyclohexene most likely resulted from attack of  $\text{RO}\cdot$  and  $\text{ROO}\cdot$  radicals on the olefin, followed by hydrogen elimination and double bond formation. Both oxy and peroxy radicals are present in the reaction mixtures from the metal catalyzed decomposition reactions illustrated in equations 1 and 2. The 2-cyclohexene-1-one is probably present as a thermal decomposition product of the 2-cyclohexenyl-tert-butyl peroxide. This peroxide is quite thermally stable and thus the decomposition is likely occurring in the injector of the gas chromatograph during analysis rather than in the experiment itself. The 2-cyclohexene-1-ol could be formed by several mechanisms. Attack of a hydroxyl radical, generated by thermal or radical induced decomposition of the hydroperoxide, is a possible mechanism. Hydrogen abstraction by a cyclohexenyl oxy radical generated by decomposition of the peroxide is also possible. It is not possible from these data to determine which mechanism is occurring under our reaction conditions.

The high yield of 2-cyclohexenyl-tert-butyl peroxide compared to the yield of the ether was surprising as both  $\text{RO}\cdot$  and  $\text{ROO}\cdot$  radicals should be present if the cycle shown in equations 1 and 2 was operative. The higher yield of the peroxide suggest a second

process is occurring in which the  $\text{RO}\cdot$  radicals are converted to  $\text{ROO}\cdot$  followed by reaction with cyclohexene. A likely mechanism for this reaction is the hydroperoxide oxidation of the oxy radical<sup>11</sup>,



This reaction apparently is faster than the reaction of the  $\text{RO}\cdot$  radical with cyclohexene.

In the absence of added ligand, a relative ranking of the activity of the catalyst in the order  $\text{V(V)} \gg \text{Co(III)} > \text{Fe(III)} > \text{Cu(II)} > \text{Ni(II)}$  was obtained (Table 1). All of the ligands reduced the activity of the vanadium catalyst and increased the activity of nickel. Apparently the ligands present in the vanadium experiment compete for coordination sites on the metal, either as free ligand or as an oxidized species (amine oxide, sulfoxide, etc.), and thereby decrease the ability of the catalyst to complex the hydroperoxide and initiate oxidation<sup>12</sup>. In the case of the nickel catalyst, the opposite effect is observed. The ligands can modify the catalyst's solubility, redox potential, etc., with a resulting increase in activity. The results with the other metals were mixed with some ligands promoting oxidation while others inhibited it. For copper, the oxidation of cyclohexene by  $t\text{-BuOOH}$  has been studied in the absence of added ligand<sup>13</sup>. A copper naphthenate catalyst was used and the peroxide and ketone were the only cyclohexene based oxidation products detected. The alcohol and ether were not detected in their study, and indeed, were minor products in our study until pyridine or tetrahydrothiophene ligands were present. The ligands increased the total yield of the alcohol and ether as well as the overall yield of all cyclohexene oxidation products with copper as a catalyst. Both of the metal chelants (chelant 1 and chelant 2) decreased the amount of oxidation product obtained. These materials are used commercially as "metal deactivators" in fuels and thus the lower oxidation product yield would be expected. The total amount of material identified in the mixture containing chelant 1 was low (78%) indicating a lot of unidentified material was present. Pyridine and chelant 1 increased the activity of the iron and cobalt catalyst while tetrahydrothiophene and chelant 2 had the opposite effect. The nature of the ligand is thus important in determining if a metal catalyst is an inhibitor or a pro-oxidant.

The activity of the iron, copper and cobalt catalysts, with and without pyridine or tetrahydrothiophene ligands, in a real diesel fuel was also investigated. In this case sulfur, nitrogen etc., components of the fuel may also influence the oxidation reactions. On monitoring the samples, it was observed that very significant degradation of the samples had occurred after only 1.5 weeks storage at 43°C. The insoluble (filterable + adherent) residue values were thus obtained (Table 2) and compared to the results in Table 1. A high level of sedimentation was assumed to be indicative of a high level of oxidation occurring in the fuel. The results were surprising however, in that the sample doped with only the hydroperoxide was much more unstable than the untreated fuel, while the sample containing both hydroperoxide and cyclohexene was only slightly more unstable. This would suggest the peroxide reacts with the cyclohexene in the fuel to give soluble products, while in its absence, the hydroperoxide reacts with other fuel components to give insoluble products. Addition of the metals to these systems greatly increased the amount of residue obtained. Copper with the pyridine ligand gave particularly high values of residue. The tetrahydrothiophene ligand gave variable results, increasing sediment with iron but decreasing the level of residue with copper and cobalt.

Analysis of the phenolic components present in mid-distillate fuels has indicated a complex mixture of low molecular weight alkyl phenols are present and that these materials can have an influence on the fuels storage stability<sup>14</sup>. Coupling reactions to give biphenyldiols are postulated to be active mechanisms involved in the instability work. Metals are known catalyst for the reaction and thus their influence on the oxidative coupling a model compound, p-cresol under fuel stability test conditions was investigated. The results (Table 3) indicated all metals when mixed with p-cresol even in the absence of added hydroperoxide or ligand gave some coupled product. A relative ranking of the catalyst in the order  $V(V) > Cu(II) > Fe(III) > Co(II)$  was obtained. In this case atmospheric oxygen in the sample is the only oxidant present. With the ligands present yields were also relatively low. When the experiment was repeated with added hydroperoxide as oxidant, the yield of coupled products increased dramatically. Copper clearly was the best catalyst for the autoxidation. Not only was the yield of the bis-phenol increased, but large amounts of trimer and even tetramer were measured (Table 4). Copper has been identified previously as an excellent catalyst for this reaction in agreement with our results<sup>15</sup>. The ligands were again influential on product yield but the results were variable. All ligands decreased the yield of oxidation products when used in combination with the copper catalyst. The sample containing pyridine was unusual in that the ligand decreased the yield obtained to that obtained in the absence of catalyst. Pyridine has been found to be a poor ligand in previous studies utilizing copper-amine catalyst to oxidize phenols and the studies indicate a strong dependence of the structure of the metal complex in these systems<sup>16</sup>. Pyridine was a pro-oxidant for the iron catalyst. Higher yields of trimer in particular being obtained when the ligand was present. The commercial metal chelants were good oxidation inhibitors for this metal, however only 78.9% of the material analyzed by the GC could be identified in the sample containing chelant 1. Compounds other than bisphenyldiols etc., were formed. This is not surprising as products resulting from C-O coupling are possible as well as from addition of the ROO· radicals to the phenol ring. The influence of the ligands on the activity of the cobalt catalyst was smaller, with pyridine again acting as an antioxidant and tetrahydrothiophene acting as a pro-oxidant. The percentage of the products identified with the sample containing chelant 1 was again low indicating additional unidentified products were present. Vanadium pentoxide alone was second only to copper in its ability to catalyze the oxidation. The tetrahydrothiophene and chelant 2 did not seem to influence its activity much while chelant 1 and pyridine again lowered the amount of oxidation occurring.

Many of the above observations were not found to correlate with samples of diesel fuel treated with the reagents and stressed at 149°C for 30 min (Table 5). Using residue pad ratings as an indicator of fuel degradation, it was clear pyridine ligand was not a catalyst deactivator as observed in the above reactions. With each of the metal catalyst evaluated, the amount of residue formed on stressing the fuel was higher in the presence of pyridine. With the exception of cobalt, the two chelant ligands were the only ones which did show some improvement in the amount of residue obtained. Apparently components present in the fuel also participate in the reactions occurring to generate the residue. The p-cresol and hydroperoxide by themselves did not influence the pad ratings.

## CONCLUSIONS

The presence of ligands in a metal catalyzed oxidation of an olefin or phenol can have a large influence on product yield and distribution. The influence is, however, dependent on the metal and the species being oxidized. For example pyridine increased the yield of cyclohexene oxidation products with the copper catalyst while it decreased the yield observed with vanadium. In the phenol coupling experiment, the addition of

pyridine gave lower yields of products than did copper itself. Many of the results could also not be correlated with residue values obtained in the real fuel. Residue values did not agree well with the product yields obtained. Apparently other components of the fuel also react with the dopants altering the results.

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**TABLE 1**  
**Product Distribution in Cyclohexene Oxidations**

Catalyst	% Cyclohexene Oxidation Product Yield after 24 hrs at 43°C <sup>**</sup>					Total Identified <sup>***</sup>
	Alcohol	Ketone	Ether	Peroxide	Total	
None	0.4	0.4	0	0.1	0.9	79.9
Cu(OAc) <sub>2</sub>	0.9	1.4	0	1.0	3.3	90.5
+ Chelant 1	0	1.6	0	0.9	2.5	78.0
+ Chelant 2	0	0.2	0	0.5	0.7	95.5
+ Pyridine	2.9	9.0	0.2	1.8	13.9	76.6
+ THT	1.3	2.0	0	1.1	4.4	89.3
FeCl <sub>3</sub>	1.7	1.6	0	0.8	4.1	91.5
+ Chelant 1	0.9	6.0	0	0.4	7.3	81.6
+ Chelant 2	0.7	2.4	0	0	3.1	84.8
+ Pyridine	1.8	5.0	0.3	0.5	7.6	87.7
+ THT	1.1	1.8	0	0	2.9	81.7
Co(OAc) <sub>2</sub>	2.5	2.5	0	0.3	5.3	95.8
+ Chelant 1	1.8	6.3	0	0.3	8.4	83.5
+ Chelant 2	0.8	2.6	0	0	3.4	87.3
+ Pyridine	1.6	5.7	0.1	0	7.4	85.0
+ THT	2.4	2.6	0	0	5.0	92.1
V <sub>2</sub> O <sub>5</sub>	0	21.4	0	1.5	22.9	96.9
+ Chelant 1	2.0	5.1	0	0.8	7.9	78.9
+ Chelant 2	1.8	3.1	0	2.4	7.3	79.1
Pyridine	0.6	1.4	0	0	1.0	99.6
+ THT	1.1	8.4	0.3	0.8	10.6	95.2
Ni(OAc) <sub>2</sub>	0.4	0.4	0	0	0.8	99.3
+ Chelant 1	2.1	4.2	0	0.4	6.7	83.8
+ Chelant 2	0.7	3.1	0	0	3.8	79.7
+ Pyridine	0.4	0.5	0	0	0.9	98.7
+ THT	0.7	1.0	0	0	1.7	97.7

\* Alcohol = 2-cyclohexene-1-ol; Ketone = 2-cyclohexene-1-one; Ether = t-butoxy-2-cyclohexene; Peroxide = cyclohexenyl-tert-butyl peroxide.

\*\* Sum of acetone, t-butanol, cyclohexene and alcohol, ketone, ether and peroxide cyclohexene derivatives yields.

**TABLE 2**  
**Fuels Stability Studies Utilizing Cyclohexene, Hydroperoxide,**  
**Metal Catalyst and Various Ligands**

Dopant	Insoluble Residue (mg/100 mL) *
None	0.3
Cyclohexene	0.3
t-BuOOH	1.7
Cyclohexene + t-BuOOH	0.5
+ FeCl <sub>3</sub>	6.1
+ FeCl <sub>3</sub> + Pyridine	3.4
+ FeCl <sub>3</sub> + THT	19.0
+ Cu(OAc) <sub>2</sub>	13.0
+ Cu(OAc) <sub>2</sub> + Pyridine	32.0
+ Cu(OAc) <sub>2</sub> + THT	9.3
+ Co(OAc) <sub>2</sub>	2.0
+ Co(OAc) <sub>2</sub> + Pyridine	2.9
+ Co(OAc) <sub>2</sub> + THT	1.9

\* After 1.5 weeks at 43°C

**TABLE 3**  
**Influence of Hydroperoxide on p-Cresol Oxidation**

Catalyst	% p-Cresol Oxidation Product Yield	
	Without t-BuOOH	With t-BuOOH
None	0	2.0
Cu(OAc) <sub>2</sub>	2.7	37.2
FeCl <sub>3</sub>	1.4	10.8
Co(OAc) <sub>2</sub>	0.3	8.6
V <sub>2</sub> O <sub>5</sub>	2.8	12.8

\* After 90 min storage at 149°C. Total of dimer, trimer and tetramer products.

**TABLE 4**  
**Product Distribution in p-Cresol Oxidation**  
**by Tert-Butyl Hydroperoxide**

Catalyst	% Oxidation product Yield *				Total Identified **
	Dimer	Trimer	Tetramer	Total	
None	2.0	0	0	2.0	99.8
Cu(OAc) <sub>2</sub>	22.9	9.5	4.7	37.2	94.8
+ Chelant 1	8.2	2.2	2.5	12.9	91.4
+ Chelant 2	11.8	4.8	3.5	20.0	99.0
+ Pyridine	3.4	0	0	3.4	96.5
+ THT	6.5	1.9	0	8.4	95.1
FeCl <sub>3</sub>	10.4	0.4	0	10.8	97.5
+ Chelant 1	1.3	1.0	0	2.3	78.9
+ Chelant 2	5.1	0	0	5.1	95.0
+ Pyridine	12.6	3.1	0	15.7	96.6
+ THT	9.3	1.7	0	11.0	91.5
Co(OAc) <sub>2</sub>	4.2	4.4	0	8.6	90.4
+ Chelant 1	6.1	0.5	0.1	6.7	82.5
+ Chelant 2	7.6	0.9	0	8.5	95.1
+ Pyridine	4.0	0.4	0	4.4	93.0
+ THT	6.8	4.8	0	11.6	69.6
V <sub>2</sub> O <sub>5</sub>	10.7	2.1	0	12.8	88.6
+ Chelant 1	6.5	0.9	0	7.4	80.0
+ Chelant 2	11.1	2.0	0	13.1	91.4
+ Pyridine	6.0	0.6	0	6.6	93.0
+ THT	10.9	1.4	0	12.3	87.1

\* After 90 min at 149°C.

\*\* Sum of t-butanol, p-cresol, dimer, trimer and tetramer yields.

TABLE 5

Dopant	Residue Pad Rating <sup>*</sup> Without t-BuOOH	Residue Pad Rating With t-BuOOH
None	4	4
p-Cresol	4	4
+ Cu(OAc) <sub>2</sub>	5	20
+ Chelant 1	4	3
+ Chelant 2	4	3
+ Pyridine	5	20
+ THT	5	17
+ FeCl <sub>3</sub>	14	11
+ Chelant 1	7	3
+ Chelant 2	4	4
+ Pyridine	15	16
+ THT	17	15
+ Co(OAc) <sub>2</sub>	4	3
+ Chelant 1	5	3
+ Chelant 2	3	7
+ Pyridine	4	8
+ THT	3	4
+ V <sub>2</sub> O <sub>5</sub>	4	4
+ Chelant 1	3	3
+ Chelant 2	3	4
+ Pyridine	4	7
+ THT	3	4

<sup>\*</sup> After 90 min storage at 149°C. Pad rating scale; 1 = clean pad to 20 = heavy residue.